

who had obtained from them a diatonic scale of an octave and a quarter in extent.

The Librarian reported the completion of his MS. condensed copy of the early records of the Proceedings of the Society from 1744 to 1837. The subject of printing the same was referred to the Committee of Five (Phillips, Horn, Lewis, Brinton and Law) appointed December 16, 1881.

And the meeting was adjourned.

On the Measurement of Electromotive Force. By George F. Barker.

(Read before the American Philosophical Society, January 19, 1883.)

The term electromotive force is applied to that force which tends to set electricity in motion. It appears to have been used first by Ohm, who in 1827 gave precision to the study of electric currents by formulating his well known law:—The strength of an electric current is directly proportional to the sum of the electromotive forces and inversely proportional to the sum of the resistances in the circuit.

The measurement of electromotive force may be absolute or relative; absolute when it is determined directly, relative when its value is obtained by comparison, the ratio of an unknown to a known electromotive force being the object of the measurement. In both measurements, the final standard of electromotive force is an absolute unit, based upon the fundamental units of mass, length and time; since these are respectively the centimeter, the gram and the second, absolute units are often called C. G. S. units. In electrostatics, electromotive force and difference of potential are synonymous, the same unit being used for both. The unit difference of potential exists between two points, when to carry a unit of positive electricity from one to the other, requires the expenditure of a unit of work; or in the C. G. S. system, of an erg. Now a unit of work, *i. e.*, an erg, is done when a unit of force, *i. e.*, a dyne, overcomes resistance through an unit of distance, *i. e.*, a centimeter. And a unit of force, *i. e.*, a dyne, is that force which produces a unit of velocity in a unit of time; *i. e.*, produces an increase of velocity of one centimeter in one second. Since in this latitude, gravity produces a velocity of about 980 centimeters per second, the force of a dyne corresponds to the attractive force which the earth exerts upon the 1-980th part of a gram. To raise one gram therefore to the height of one centimeter requires the expenditure of 980 ergs of work. Obviously then if two electrified bodies at unit distance attract or repel each other with a force equivalent to that which

the earth exerts on a gram weight, there exists between them a difference of potential of 980 absolute units. By measuring the force between two electrified bodies in grams, the difference of potential or the electromotive force between them is easily calculated in absolute measure. By multiplying this value in electrostatic units, by thirty thousand million, the electromotive force is obtained in absolute electromagnetic units.

The instrument used for measuring differences of potential is called an electrometer ; if by direct measurement, an absolute electrometer. The absolute electrometer of Sir William Thomson is the best thus far devised. This instrument consists of two metal plates, one of which, the smaller, is provided with a guard ring so that the electrical distribution shall be uniform ; these plates being so arranged that the attraction between them may be very accurately measured. The force may be measured at a constant distance by varying the weight necessary to balance it ; or the distance may be varied until the force balances a constant weight. The latter method is preferred in the absolute electrometer of Thomson. With this instrument, the electromotive force of a Daniell cell was found to be 0.00374 electrostatic unit, corresponding to 112 million electromagnetic units.

Relative measurement of electromotive force, especially for practical purposes, is much more frequent than absolute measurement. Although the same units may be used, yet in practice it has been found more convenient to employ a separate unit called the volt, the value of which is given as one hundred million absolute electromagnetic units. Moreover, this unit is represented not in the abstract form alone, but also concrete. Some distinct electromotor, the difference of potential between the electrodes of which has been accurately measured, is taken as the standard. For example, the Daniell cell above mentioned has an electromotive force, by the definitions already given, of 1.12 volts. Such a battery, used for measurement, is called a standard battery.

For determining an unknown electromotive force, it is only necessary to determine the ratio between this and the electromotive force of the standard battery. Two general methods of doing this are in use ; the one direct, the other indirect. In the direct method, an electrometer which has been calibrated is employed ; *i. e.*, one whose constants have been determined by comparison either with the standard battery or with an absolute instrument. Such are the portable and the quadrant electrometers of Thomson. In the latter instrument an 8-shaped needle of aluminum swings in a cylindrical metal box with separated quadrants. The alternate quadrants are electrically connected when the instrument is in use. A small charge being communicated to the needle—previously adjusted so that its axis is parallel to the line between adjacent quadrants—any electrification of the quadrants is made apparent by the motion of the needle to the right or left. By connecting these quadrants, first with the electrodes of the standard cell, and then with the cell whose electromotive force is to be measured, the ratio of the deflections gives the ratio of the electromo-

tive forces, provided the angle of rotation be small. A mirror attached to the suspension of the needle enables these deflections to be accurately read with a telescope and scale. A simpler instrument suffices when the zero method is employed. In this case the two electromotors are simultaneously connected to the quadrants, their electrodes being reversed. If equal, the deflection will be zero. If unequal, it will be equal to the difference. By varying the known electromotive force until the deflection is zero, the two are again equal.

While, in the direct method, the electromotive force is the quantity which is measured, in the indirect method some other quantity or quantities are measured, and the electromotive force deduced by calculation from the known relation between the quantities. When, for example, the current strength is measured on the galvanometer and the resistance of the circuit is known, the law of Ohm enables the electromotive force to be computed. In Wiedemann's method, the electromotor to be measured is joined up with the standard battery, in circuit with a galvanometer, first with the electrodes in the same direction, then reversed. The electromotive force required is then the product of the standard electromotive force by the quotient of the difference of the current strengths divided by the sum. Another method consists in putting the standard cell in circuit with a galvanometer, the resistances of both being known. The standard cell is then replaced by the electromotor to be tested and the resistance in circuit varied until the same deflection is obtained. The electromotive force of the standard cell multiplied by the ratio of the second total resistance to the first gives the electromotive force required. The electrometer methods have the advantage of not using the current of the electromotor to be measured; and hence any change in its condition due to the current produced is avoided.

From what has been said, it will be evident that the selection of the standard cell is a matter of prime importance. The advantages of the Daniell cell for this purpose are too well known to require elaborate statement here. As used on closed telegraphic circuits and the like, two forms have come into general favor. One of these is that employed originally by Professor Daniell. It consists of a glass jar containing copper sulphate, in which the copper plate is immersed, and of a porous cup containing the zinc plate, a more or less dilute solution of zinc sulphate. The other form is the modification first proposed by Varley and afterward by Callaud, in which the porous cup is done away with, the differing densities of the two solutions being depended upon to keep them separated. The copper sulphate solution is placed at the bottom of the jar in contact with the copper plate. As the density of this solution when saturated is 1.186 at 15° C. the solution of zinc sulphate ordinarily rests upon it and in contact with the suspended zinc plate. But as the action of the battery goes on and the zinc sulphate accumulates in the solution, this later finally becomes heavier than the copper sulphate solution (the density of a saturated solution of zinc sulphate being 1.44 at 15° C.), and

falls to the bottom ; thus reversing the normal conditions in the battery. In 1871 Sir Wm. Thomson attempted to reverse the position of the plates in this gravity battery and place the zinc at the bottom in contact with the heavier solution. But the collateral disadvantages arising from the change more than balanced the advantages. He returned to the old form, therefore, but arranged a siphon in such a way that the zinc sulphate solution should be gradually withdrawn and too great concentration avoided. In practice the zinc sulphate should never be allowed to accumulate so as to increase the density of the solution above 1.17. This may be accomplished readily by pouring off the solution from the top of the jar and replacing it by pure water. When freshly set up, both of the forms of battery above described require to be kept on closed circuit for a day or two. Their condition of equilibrium is then reached and they may be used for the determination of electromotive force.

The difference of potential between the electrodes of a Daniell cell has been determined by many experimenters; by Regnault, by Poggendorf, by Buff, by Beetz, by Petruschefsky, by Clark and Sabine, and by Ayrtton and Perry, among others. They find that while it varies somewhat under variations of condition, yet that on the whole, it is remarkably constant, the maximum being 1.081 and the minimum 0.901 volt. In all these experiments the copper was immersed in a saturated solution of copper sulphate. The zinc was placed in solution of sodium chloride, in dilute sulphuric acid or in solution of zinc sulphate, all of varying strengths in the different experiments. It is noticeable that in none of these measurements made by indirect methods is the electromotive force as high as that already mentioned as having been obtained by Sir William Thomson by means of his absolute electrometer. Since the electromotive force of a Daniell cell is the sum of the differences of contact-potential within it, it would seem that any variation in the value of this electromotive force must be due either to a change in the character or concentration of the solutions, or to a difference of temperature. Moreover it has been observed that the electromotive force of the gravity form of battery is always a little higher than that of the cell in which a porous cup is used ; a result due, probably, to the different conditions under which the diffusion of the two liquids takes place, a fact pointed out by J. W. Draper in 1834.

Using, therefore, the same form of battery, the solutions being always the same in kind and in concentration, and the temperature being the same, it is fair to infer that the Daniell cell may be made sufficiently constant to serve as a reliable standard of electromotive force. Several attempts have been made to do this. Raoult in 1864 (*Ann. Chim. Phys.*, IV, ii, 345), proposed a standard cell consisting of two covered jars of glass, one containing a copper plate in a saturated solution of copper sulphate, the other a zinc plate in a solution of zinc sulphate in an equal weight of water. The two were connected by an inverted U tube, whose ends were closed by porous plates of earthenware cemented to them. By

means of a tubulure in the bend this tube was filled with the zinc sulphate solution. When not in use, the U tube is removed and kept in a separate vessel. Kempe in 1880 (*J. Soc. Teleg. Eng.*, June, 1880), described a standard Daniell cell which has been adopted in the British Post-Office. The containing vessel is of porcelain, having two compartments. In one of these is a half saturated solution of zinc sulphate, reaching to the lower edge of the zinc plate. In the other is a flat, porous cup containing the copper plate surrounded with crystals of copper sulphate, and immersed in copper sulphate solution. To use this battery, the porous cup is transferred from one compartment to the other, thus raising the zinc solution into contact with the zinc plate. After making the measurement, the porous cup is replaced in its own compartment. Any copper which may have been carried into the zinc solution is precipitated upon a fragment of zinc kept constantly in it.

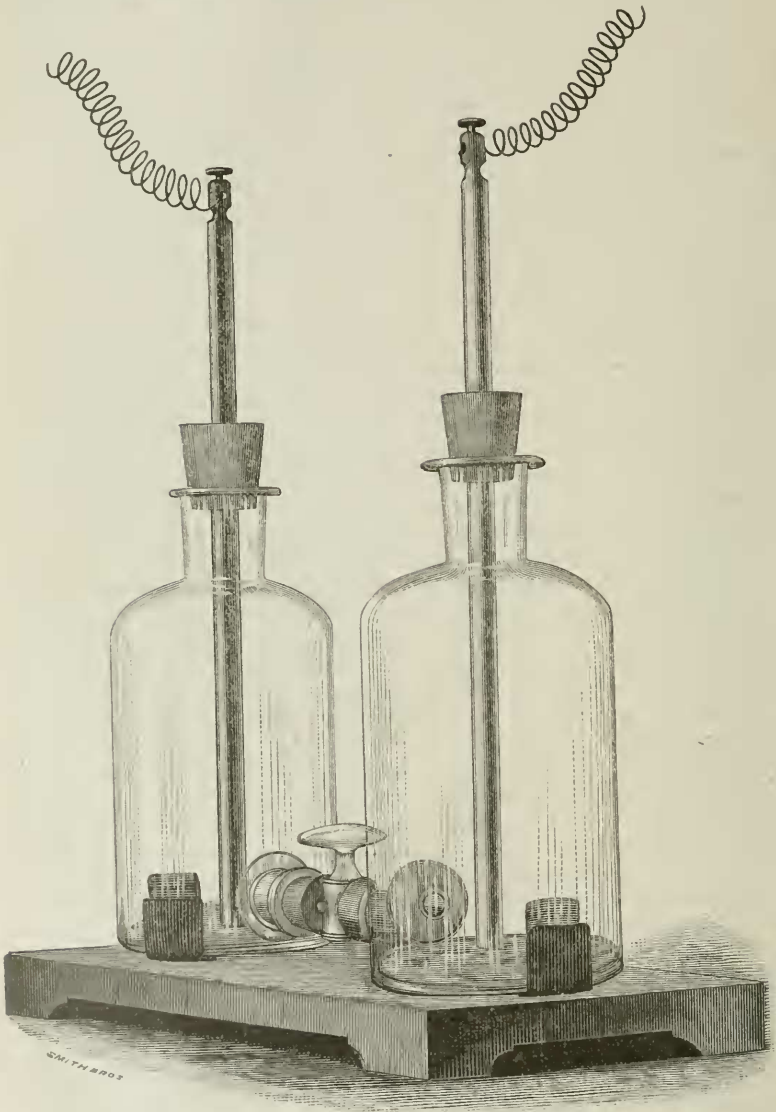
Having had occasion for a series of months, at intervals, to make measurements of electromotive force by the method of comparison, I have been led to devise a form of standard Daniell cell which appears to have so important advantages over others heretofore used as to justify me in bringing it to the notice of the Society. The form of apparatus which has been adopted is represented in the annexed wood-cut. It consists of two bottles with lateral tubulures near the bottom. These are closed with rubber corks through which passes a stop-cock of glass. The necks of the bottles also carry corks of rubber, through which pass the rods of zinc and copper. The bottle containing the rod of zinc is filled about three-fourths with a solution of zinc sulphate saturated at 15° C. That containing the copper rod with a saturated solution of copper sulphate. When the cell is to be used for measurement, the cock is opened and the two liquids are thus put in communication. At the end of the experiment, it is again closed and all diffusion is prevented.* For ordinary use, especially where a large number of cells in series is required, a much cheaper apparatus may be constructed. Those set up in my own laboratory consist of a couple of the cheap bottles now in general use for the nasal douche and for containing dry plate developers, which have a small lateral spout at the bottom. Over these a rubber tube may be passed and tied, being closed when required by a wire compressor. In practice I have found it an advantage to place a wisp of spun glass in the rubber tube to prevent adherence between its sides. The zinc and the copper rods pass through corks in the mouths of the bottles as before.

The advantages which are claimed for this new form of cell are :

1st. Its constancy. When set up, all such cells are identical. The zinc is in contact with a solution of zinc sulphate, and the copper with one of copper sulphate both saturated at 15° C. Moreover, this identity continues. When on closed circuit, the liquids are altered by diffusion to a scarcely appreciable extent, the surface of contact being so small. During action copper sulphate is decomposed on one side and cop-

The cell here represented was made for me by J. W. Queen & Co., of this city.

per deposited ; zinc is dissolved on the other side and zinc sulphate produced. The amount of current used in a measurement is small, first be-



cause the internal resistance of the cell is high, and second because the duration of the test is brief. But the minute change thus caused in the

solution is prevented, first, by keeping a crystal of copper sulphate in the copper solution, and second, by the deposition of the excess of zinc sulphate in crystals. Since the zinc solution is the heavier, any hydrostatic transfer will be into the copper solution where no damage is done. When the cell is on open circuit, no diffusion takes place, communication being cut off. And since the apparatus is wholly closed to the air, no change in the conditions can arise from evaporation. Provided therefore the temperature be uniform, the electromotive force of the cell may be expected to be constant within narrow limits.

2d. Its transportability. In the use of the ordinary Daniell cell, particularly of the gravity pattern, any change of position disturbs more or less the conditions of equilibrium, and so varies the electromotive force. After moving such a cell, therefore, or after altering in any way its normal state, as by adding water lost by evaporation, it is necessary to allow twenty-four hours or more of rest, before the battery can be trusted to give proper measurements. But in the cell now proposed, no change can take place in its conditions by being moved from place to place. Hence for local testing in circumstances where a permanent battery cannot be had, its value is considerable.

3d. Its convenience and cheapness. The common form of Daniell battery requires to be especially prepared for use. If set up anew, twenty-four hours are needed before it comes into good working action. Even the improved forms of standard cell above described are more or less inconvenient, since they require something to be done to put them in action. But in the form now proposed the cell is always ready for use, no matter how long a time may have elapsed since it was used before. The opening of a stop-cock puts it in full operation. Moreover, this cell is readily constructed from apparatus and material at hand in every laboratory. And if douche bottles are used, the cost is not over a dollar.

It is evident that the form of apparatus now described has a much wider range than has yet been claimed. By its means not only may the effect of using various solutions in contact with either plate of a Daniell cell be accurately studied, free from many of the disturbing causes hitherto encountered, but by the use of various metals also, the innumerable questions of importance, concerning not only primary but also secondary batteries, may be conveniently investigated. One of these for example, is the question whether the zinc of a Daniell cell should be amalgamated. The impression is very generally in favor of amalgamation, since in a zinc sulphate solution amalgamated zinc is said not to become polarized; and since the electromotive force is one or two per cent. higher. But experiments have shown, that while amalgamated zinc should be used when the solution is acid, yet that when it is neutral, local action is greater with amalgamated than with unamalgamated zinc.

Experiments now in progress with this new form of cell, it is hoped, will enable some of these doubtful points to be satisfactorily settled.

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